trum. This occurs in the range 760–950 cm^{-1} in simple ionic peroxides[26] and in the range 800–940 cm^{-1} in a variety of transition metal–peroxo complexes.[27] The superoxide O–O stretch is observed at 1140–1150 cm^{-1} in KO_2 and RbO_2.[28] There is now a multitude of contradictory Raman spectra of $YBa_2Cu_3O_7$ in the literature,[29] but none exhibit bands in the peroxide stretching region. One single paper[30] reports a weak, broad band in the superoxide region near 1100 cm^{-1}, but the spectrum in this report is not representative of the spectra in other reports.[29] It is difficult to obtain reliable Raman spectra of highly absorbing black solids with visible light, and the variable literature results may reflect different surface impurities on individual samples. We attempted to record the Raman spectrum of $La_2NiO_{4.135}$, whose oxidized species has been assigned as peroxide.[16] Only a very weak peak at 996 cm^{-1} was observed at the same position as a weak background signal present in the glass capillary cell. There are no conclusive Raman data supporting the assignment of peroxide species in the solid state.

In conclusion, our experiments offer no support for the idea that peroxide is present in $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, or La_2NiO_4. The destruction of peroxide in solution when these compounds dissolve might be indicative of Cu^{3+} or Ni^{3+}.

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Registry No. $YBa_2Cu_3O_{6.85}$, 110584-09-3; $La_{1.8}Sr_{0.2}CuO_4$, 107499-44-5; La_2CuO_4, 12053-92-8; $La_2NiO_{4.14}$, 119325-54-1; $BaCuO_{2.05}$, 119325-55-2; Y_2O_3, 1314-36-9; $BaCO_3$, 513-77-9; CuO, 1317-38-0; La_2O_3, 1312-81-8; $SrCO_3$, 1633-05-2; NiO, 1313-99-1; BaO_2, 1304-29-6; $KMnO_4$, 7722-64-7; KO_2, 12030-88-5; $YBa_2Cu_3O_{6.90}$, 108470-72-0; $CuSO_4$, 7758-98-7; $NiSO_4$, 7786-81-4.

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Hydroxide-Induced Reduction of Elemental Sulfur (S8) to the Trisulfur Anion Radical (S3·−)
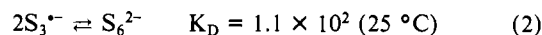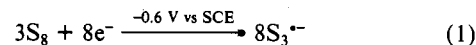
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In aprotic solvents hydroxide ion reacts with elemental sulfur (S_8) to give the trisulfur anion radical S_3·$^-$ as the major product. The reaction stoichiometry (eight $^-$OH per three S_8 to give eight

Scheme I
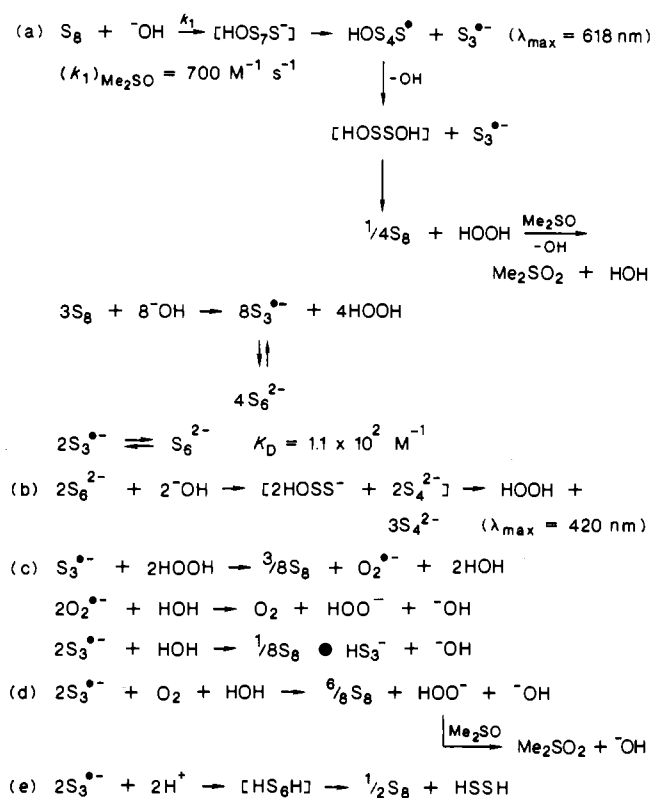
S_3·$^-$) is consistent with the results for the electrochemical reduction of S_8 in dimethyl sulfoxide[1,2] and in acetonitrile.[3]

$$3S_8 + 8e^- \xrightarrow{-0.6 \text{ V vs SCE}} 8S_3\cdot{}^- \quad (1)$$

$$2S_3\cdot{}^- \rightleftarrows S_6{}^{2-} \quad K_D = 1.1 \times 10^2 \ (25 \ ^\circ C) \quad (2)$$

Dissolution of alkali polysulfides in hexamethylphosphoramide also yields substantial amounts of S_3·$^-$.[4]

Although the hydroxide ion induced formation of S_3·$^-$ from S_8 is unique in our experience, several previous observations were brought to our attention by a helpful reviewer. A blue color was noted when elemental sulfur was heated with alkaline water[5,6] and when S_8 was dissolved in KOH–acetone solutions.[7] This blue species, which has been identified as S_3·$^-$,[1,8] also resulted when partially hydroxylated MgO was combined with S_8.[9] Polysulfides ($S_n{}^{2-}$) in aprotic solvents undergo dissociation and disproportionation reactions to yield S_3·$^-$,[10] and it is formed from the reaction of HS^- with S_8.[11]

A recent study[12] has demonstrated that hydroxide ion ($^-$OH) in acetonitrile reduces anthraquinone to its anion radical (AQ + $e^- \rightleftarrows AQ\cdot{}^-$; $E^{\circ\prime}{}_{MeCN} = -0.82$ V vs SCE).

$$AQ + {}^-OH \rightarrow AQ + \frac{1}{2}HOOH \quad (3)$$
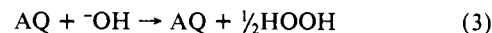
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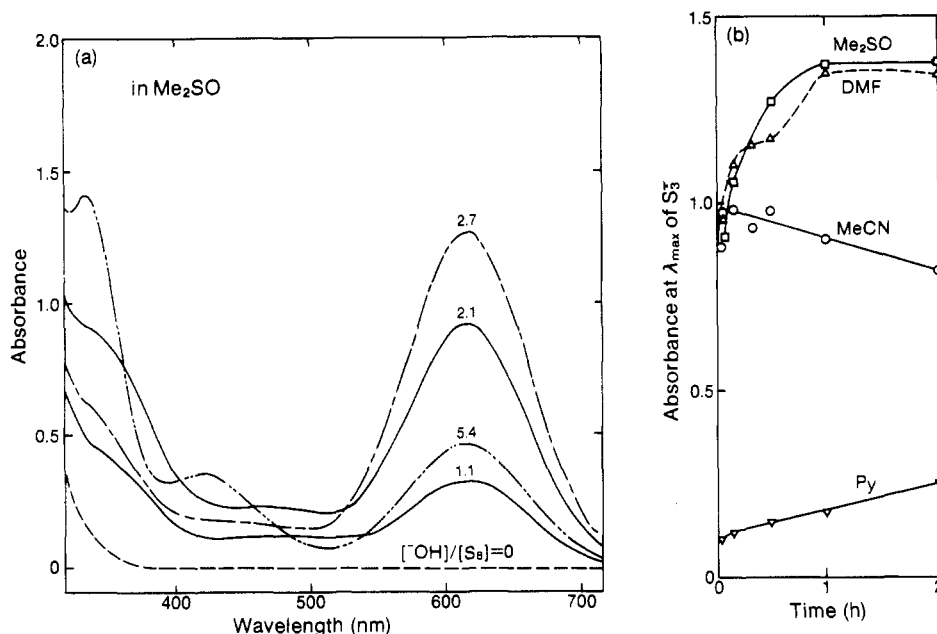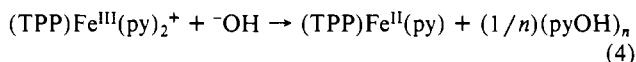
Figure 1. (a) Absorption spectra for the product solutions from the combination of $(Bu_4N)OH$ with 0.2 mM S_8 in dimethyl sulfoxide. The initial mole ratios are indicated on the curves, and the data were recorded 10 min after mixing at 25 °C. (b) Absorbance at λ_{max} as a function of time after combining 2.7 ⁻OH ions per S_8 molecule (0.2 mM) in the indicated solvents. The initial absorbance was zero for each solution, and λ_{max} was as follows: Me_2SO, 618 nm; DMF, 618 nm; py, 616 nm; and MeCN, 612 nm.

In pyridine ⁻OH also reduces (*meso*-tetraphenylporphyrinato)-iron(III) via electron transfer[13]

$$(TPP)Fe^{III}(py)_2^+ + {}^-OH \rightarrow (TPP)Fe^{II}(py) + (1/n)(pyOH)_n \quad (4)$$

Thus, the propensity of ⁻OH to act as an electron-transfer agent [when its conjugate oxidant (·OH) is stabilized by bond formation (HO–OH or py–OH)] appears to be general.[14]

Figure 1a illustrates the spectra for S_8 and for the product solutions from the combination of various mole ratios of ⁻OH with S_8 in dimethyl sulfoxide. The absorption band at 618 nm, which is characteristic of $S_3^{·-}$ (ϵ 4.5 × 10^3 M^{-1} cm^{-1}),[1,8] can be used to determine the reaction stoichiometry (2.7 ⁻OH per S_8). Addition of excess ⁻OH results in the loss of $S_3^{·-}$ and the appearance of a band at 420 nm that is due to S_4^{2-} (also observed when ⁻OH or excess electrons are added to $S_3^{·-}$ in an electrolysis experiment).[1] The dynamics for the reaction (2.7 ⁻OH ions per S_8 molecule) in several aprotic solvents are illustrated in Figure 1b. Although all of the initial rates of formation for $S_3^{·-}$ are fast, a stable stoichiometric yield of $S_3^{·-}$ only results when Me_2SO is the solvent. The conjugate oxidant of ⁻OH is ·OH or HOOH, which can react with the solvents and $S_3^{·-}$. The reaction stoichiometry for HOOH with electrosynthesized $S_3^{·-}$ is 2:1 to yield S_8, O_2, and base. Under alkaline conditions, Me_2SO reacts rapidly with HOOH to give Me_2SO_2 and HOH,[15] but the other solvents are degraded to a variety of reactive intermediates.[12,16] Solutions of $S_3^{·-}$ in Me_2SO react rapidly with O_2 to give S_8 and ⁻OH.

Measurement of the initial rates of formation for $S_3^{·-}$ (d-$[S_3^{·-}]/dt)_{t=0}$ when various ⁻OH/S_8 mole ratios are combined indicates that the reaction is first order in S_8 and first order in ⁻OH and that the initial step is rate limiting. For the rate law

$$d[S_3^{·-}]/dt = k_{obs}[^-OH][S_8] \quad (5)$$

k_{obs} has an average value of $(2 \pm 1) \times 10^3$ M^{-1} s^{-1} in Me_2SO at 25 °C. If a stoichiometric factor of 2.7 is used, the rate constant for the initial step (k_1) is $(7 \pm 4) \times 10^2$ M^{-1} s^{-1}.

The results are summarized in Scheme I, and stoichiometric relationships are proposed that are in accord with independent titrations of the suggested intermediates. Section a represents the overall stoichiometry and the observed material balance for the reaction in Me_2SO. Although the inferred reaction path is reasonable, the mechanism clearly is complex with many dissociations and disproportionations. In Me_2SO, side products that would result from an ·OH intermediate were not detected. The parallel between the one-electron adduct of elemental oxygen ($O_2^{·-}$, superoxide ion) and the product from the one-electron reduction of elemental sulfur ($S_3^{·-}$ trisulfur anion radical) is striking [stable anion radicals from electron addition to the stable elemental molecules (S_8 and O_2)]. Perhaps this is the most compelling example that ⁻OH represents a stabilized electron and can affect the electron-transfer reduction of a non-metal to give an anion radical ($S_3^{·-}$). Because $S_3^{·-}$ is the chromophore in the mineral lapis lazuli,[17] the chemistry of Scheme I may be the basis for its geological formation.

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